Journal of Hazardous Materials 171 (2009) 606–612

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Continuous electrolytic decarbonation and recovery of a carbonate salt solution from a metal-contaminated carbonate solution

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ARTICLE INFO

*Article history:*
Received 4 February 2009
Received in revised form 4 May 2009
Accepted 10 June 2009
Available online 18 June 2009

*Keywords:*
Continuous
Electrolytic
Decarbonation
Recovery
Stacked-cell
Carbon dioxide

ABSTRACT

This work studied the characteristic changes of a continuous electrolytic decarbonation and recovery of a carbonate salt solution from a metal-contaminated carbonate solution with changes of operational variables in an electrolytic system which consisted of a cell-stacked electrolyzer equipped with a cation exchange membrane and a gas absorber. The system could completely recover the carbonate salt solution from a uranyl carbonato complex solution in a continuous operation. The cathodic feed rate could control the carbonate concentration of the recovered solution and it affected the most transient pH drop phenomenon of a well type within the gas absorber before a steady state was reached, which caused the possibility of a $CO_2$ gas slip from the gas absorber. The pH drop problem could be overcome by temporarily increasing the $OH^-$ concentration of the cathodic solution flowing down within the gas absorber only during the time required for a steady state to be obtained in the case without the addition of outside NaOH. An overshooting peak of the carbonate concentration in the recovered solution before a steady state was observed, which was ascribed to the decarbonation of the initial solution filled within the stacked cells by a redundant current leftover from the complete decarbonation of the feeding carbonate solution.

## 1. Introduction

A great deal of interest has recently been shown on a uranium-leaching from spent nuclear fuel in a high alkaline carbonate media instead of an acid media to enhance its safety, economic competitiveness, and to minimize the generation of secondary waste streams [1–5]. When a carbonate solution is used to treat nuclear spent fuel or uranium ore, a large amount of carbonate salt such as $M_2CO_3$ ($M = Li^+, K^+, Na^+, NH_4^+$) is used. Therefore, if the carbonate salt is not recycled in the process using carbonate solutions, an enormous amount of carbonate salt would be accumulated, which weakens the advantages and the environmental friendliness of the process using a carbonate solution. The carbonate solutions used in those systems may contain metal–carbonate complex ions or be mixed with several impurity metal ions.

Our previous works studied the batch operation characteristics of an electrolytic system consisting of a cation exchange membrane-equipped cell and a gas absorber to recover the carbonate salt solution for recycle from a uranyl peroxo carbonato complex solution [6]. In the system, the uranium-complexed carbonate solution was acidified in the anodic chamber by $H^+$ ions generated through the water split reaction to release $CO_2$ gas from the solution, while the uranium ions were left in the anodic chamber. The released $CO_2$ gas was recovered as a carbonate salt solution again by the $OH^-$ ions generated through the water split reaction in the cathodic chamber and by the migration of the cations composed of the carbonate salt, which remained after the decarbonation in the anodic chamber. In our previous work, the decarbonation was elucidated to be proportional to the total electric charge supplied to the system, and the constant current operation was found to be better than the constant voltage operation from an energy consumption point of view.

In order to apply an electrolytic recycling system into actual cases [1,2,5,6], the continuous operation characteristics of the system should be studied, but experiments for that have not been carried out yet. Accordingly, in this work, a once-through decarbonation and a recovery of carbonate salt solution from a uranyl carbonato complex solution by using a system which consisted of a multi-cell-stacked electrolytic system equipped with cation membrane and a gas absorber were studied with several variables of the applied current density, anodic and cathodic flow rates, and so on.

## 2. Experimental

A schematic diagram of the electrolytic system used in this work for the electrolytic decarbonation and recycling of a carbonate salt from a uranium-containing carbonate solution is shown in Fig. 1. The electrolytic system consisted of a three cell-stacked

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doi:10.1016/j.jhazmat.2009.06.043

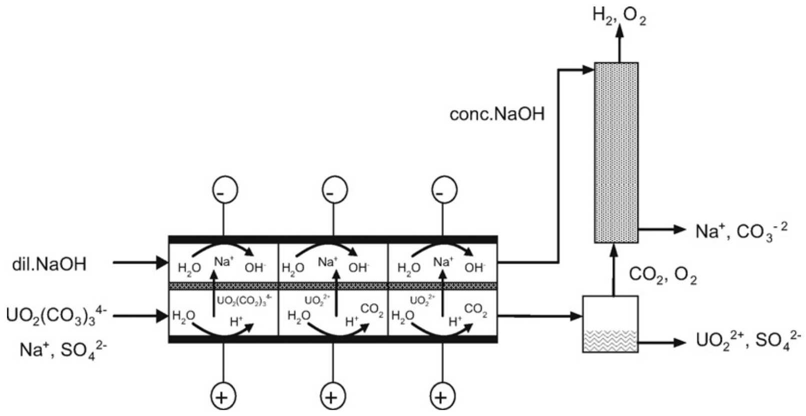

**Fig. 1.** Schematic diagram of an apparatus used for electrolytic decarbonation and recycling of a sodium carbonate salt from uranyl peroxo carbonato complex solution.

electrolyzer and a $CO_2$ gas absorption column for a gas–liquid contact. In the electrolytic system, the anolyte and catholyte flowed independently in series through the respective anodic and cathodic chambers of the stack. The volumes of the anodic and cathodic chambers of each cell were about 22 ml. A line for discharging gas from a gas–liquid separator, where the final anolyte coming out of the electrolyzer went into, was connected to the bottom end of the $CO_2$ gas absorber mounted outside the electrolyzer, and the final catholyte coming out of the electrolyzer was introduced to the top end of the $CO_2$ gas absorber. Each cell of the cell-stacked electrolyzer had an anode of $IrO_2$ and a cathode of Ti and was divided by a cation exchange membrane (Nafion 424). The size of each electrode was W 2 cm × H 4 cm × T 0.1 cm of a Madras type with a mesh size of 6 mm× 12 mm. The gas absorber was prepared by packing a Pyrex glass tube of 40 cm in length and 2.5 cm in diameter with silica beads of 1 mm in diameter. The void fraction of the packed column was about 40%. In our preliminary experiments, the column was confirmed to be able to completely absorb the $CO_2$ gas released from the anodic chamber.

For the experiments of an electrolytic decarbonation and recovery of the carbonate salt solution, a 0.1 M NaOH solution and a 0.5 M $Na_2CO_3$ solution (or a uranyl tri-carbonato complex ion ($UO_2(CO_3)_3{}^{4-}$) solution containing 1.0 g/l uranium in 0.5 M $Na_2CO_3$) mixed with 0.1 M $Na_2SO_4$ were used as the catholyte and anolyte solutions to be fed into the electrolyzer, respectively. The $Na_2SO_4$ in the anolyte was used as a supporting electrolyte to prevent an operational cut-off caused by a rapid increase of the cell voltage, which occurs because the conductivity of an anolyte, bearing only a carbonate salt, decreases rapidly as its electrolytic decarbonation is being progressed [6]. The uranyl carbonato complex ion solution was prepared by dissolving $UO_2$ powder in a 0.5 M $Na_2CO_3$ solution for a sufficient dissolution time. The pH values of the recovered carbonate and anolyte solutions leaving the gas absorber and the gas–liquid separator mounted outside the final anodic chamber of the electrolyzer were recorded on-line by pH-meters and a data-logger. The solutions in the anodic and cathodic chambers were sampled at regular intervals for their analyses.

The carbonate concentration was analyzed by an inorganic carbon analyzer (Shimadzu TOC-V CSH/TNM-1). The concentrations of the sulfate, sodium, and hydroxyl ions were analyzed by using an auto-titrator and an ion chromatography (Dionex ICS 90). The concentration of U was analyzed by a colorimetric method using Arsenazo III. All the chemicals used in this work were reagent grade, and they were dissolved, as received, in demineralized water of 18.2 MΩ prepared by a double distillation and an ion-exchanger (Milli-Q plus). All the experiments were carried out at room temperature.

## 3. Results and discussion

### 3.1. Background for electrolytic decarbonation of a uranyl carbonate solution and recovering a carbonate salt solution

This work is for an investigation of the characteristic changes during a continuous electrolytic decarbonation and recovery of a carbonate salt solution from a used carbonate solution containing metal ions such as uranyl carbonato complex solution. Therefore, it is necessary to understand the reactions relevant to the carbon species and the electrochemical reactions occurring in the electrolytic system, which are described in detail elsewhere [5–7]. Carbonate species are interchangeable among the carbonic acid of $H_2CO_3$, bicarbonate of $HCO_3{}^-$, and carbonate of $CO_3{}^{2-}$ species depending on the solution pH as shown in Eq. (1). Only carbonate ions exist in the solution at pH of more than 12, and only carbonic acid ($CO_2$ gas is released from the solution) does at pH of less than 4. In the range between pH 4 and 8, the carbonate ions, bicarbonate ions, and carbonic acid coexist in different mole fractions of their species, depending on the solution pH [6]. Uranyl ion of $UO_2{}^{2+}$ is known to form a uranyl tri-carbonato complex ion of $UO_2(CO_3)_3{}^{4-}$ in carbonate solution as shown in Eq. (2).

$$H_2CO_3(CO_2\uparrow) \leftrightarrow HCO_3{}^- \leftrightarrow CO_3{}^{2-} \qquad (1)$$

$$UO_2{}^{2+} + 3CO_3{}^{2-} = UO_2(CO_3)_3{}^{4-} \qquad (2)$$

From the above equations, the uranyl ions embedded in the carbonato complex ions can be considered to be separated from the carbonate species by controlling the solution pH. Fig. 2 shows the changes of the uranium concentrations in the solutions according to the pH-adjustments of the uranium solutions which were prepared by dissolving $UO_2$ powder in a carbonate solution of 0.5 M $Na_2CO_3$. An inset box of Fig. 2 shows the absorbance spectra of the prepared uranyl carbonato complex ion solution at pH 11 and the uranium solution at pH 2 after by pH-controlling the uranyl carbonato complex solution by using $HNO_3$. The spectra of the solution at pH 11 and 2 reveal the typical characteristic absorbance peaks of a $UO_2(CO_3)_3{}^{4-}$ solution at 435, 448, and 462 nm, and those of a $UO_2{}^{2+}$ solution at 404, 414, and 426 nm, respectively [1,6]. When the prepared uranyl carbonato complex solution was acidified with $HNO_3$, the uranium concentration in the solution did not change from pH 11 to 1 except for around pH 4 where a slight precipitation was observed. The solubilities of the uranyl ions in the solution with bicarbonate or carbonate ions at pH of more than 5, and in the solution free of carbonate ions at pH of less than 3 were higher than the uranium concentration of the initial carbonate solution, so that there is no change of the uranium concentration in those pH ranges. However, the solubility of uranyl ions in the solution at